



TECHNICAL NOTE

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THE PROBLEM OF NITROGEN PEROXIDE IN THE ATMOSPHERES OF PLANETS

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SUMMARY

It has been theorized that the atmospheres of Jupiter, Venus, and Mars contain nitrogen peroxide, a mixture of NO_2 and N_2O_4 . It would seem that if the mixture does exist in these atmospheres, it could continue to exist there; but it is not known how the nitrogen peroxide came to be there. There would appear to be two possible explanations — a thermal process in the early history of the planet or a special activation mechanism operating under present conditions. But there are arguments against both of these explanations. At the present time, therefore, the field is completely open to discussion and doubt.

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INTRODUCTION

Recently Kiess, Karrer, and Kiess suggested that certain strong absorption features in the spectra of Jupiter, Venus, and Mars (Reference 1) indicate the presence of nitrogen peroxide in the atmospheres of these planets. Evidently the compounds NO_2 and N_2O_4 exist in equilibrium in varying proportions as a red gas, the mixture being known as nitrogen peroxide. The aforementioned authors have furthermore demonstrated very convincingly that almost all Martian phenomena can be explained on the basis of the physical and chemical properties of these compounds. This paper discusses the origin of these oxides.

THERMODYNAMIC PROPERTIES OF NITROGEN PEROXIDE

Kiess, Karrer, and Kiess have already given a brief review of the physical and chemical properties of these oxides. However, in order to understand their formation and stability, it is also desirable to know their thermodynamic properties. Figure 1 indicates the free energies of formation (in units of kilocalories per mole) of NO (nitric oxide), NO_2 , and several compounds provided for comparison purposes, all evaluated at a temperature of 25°C and a pressure of one atmosphere. The free energy of formation of a chemical compound may be likened to the potential energy of a dynamic system. A high free energy of formation means that the compound is thermodynamically unstable, just as a high potential energy means a mechanical system is dynamically unstable.

*A part of the present investigation was carried out when the author was at the Institute for Advanced Study, Princeton, New Jersey.

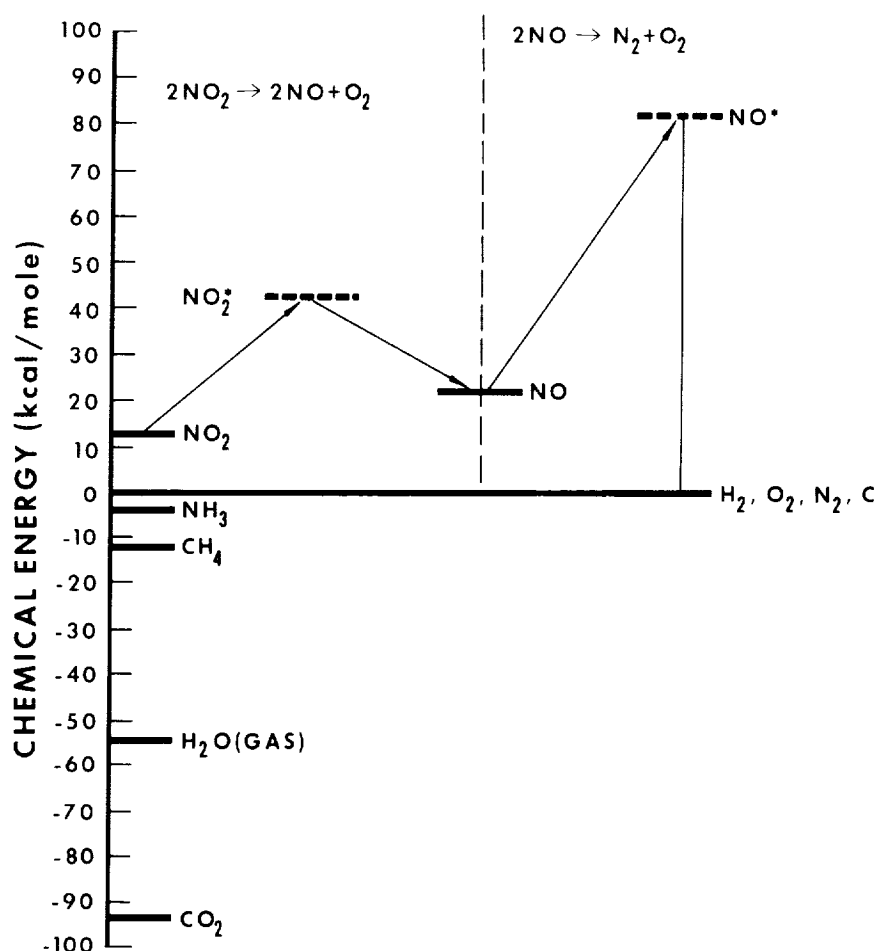


Figure 1 — Energy diagram. Free energies of formation of NO and NO_2 are compared with those of other common molecules. Also, the activation energies of NO and NO_2 are shown as a potential barrier to the dissociation reactions given in the diagram. One kilocalorie per mole is equivalent to 0.043 electron volt per molecule.

Therefore, it is obvious from Figure 1 that CO_2 , H_2O , CH_4 , and NH_3 are stable, but NO and NO_2 are not. However, this does not mean that NO and NO_2 will automatically decompose into N_2 and O_2 . In fact, at temperatures prevailing in the atmosphere of the earth, for example, NO_2 is highly stable and NO combines rapidly with O_2 to form NO_2 . The reason for the stability (at low temperatures of course) of these and other chemical compounds of positive free energies of formation becomes clear in the light of the fact that their molecules do not enter into a chemical reaction unless they are activated to a higher energy state than their normal level. This higher energy state is called the activated state and will be denoted, in this paper, by an asterisk. The additional energy required is called the energy of activation and is also expressed in terms of kilocalories per mole in Figure 1. For each chemical reaction there always corresponds a definite value of the energy of activation. Figure 1 illustrates the energies of activation of the following two reactions:



and



In order to decompose, NO_2 has first to be activated to the NO_2^* state. Energy must be available to activate the molecules before the reaction will start. Therefore the effect of the energy of activation of a chemical reaction may be compared to the effect the potential barrier has on the motion of a classical dynamic system, since if no extra energy is added to the dynamic system, the system cannot pass over the "barrier" to get to the other side.

At low temperatures the thermal energy is not large enough to activate the molecules and chemical reaction cannot take place. For this condition the composition of a mixture of gases may be regarded as frozen in an arbitrarily fixed state. For such a state the composition cannot be derived by calculations based upon thermodynamic equilibrium. As an example consider a mixture of H_2 , O_2 , and H_2O . In a state of thermodynamic equilibrium H_2O would be expected to be the dominant ingredient. But, without an exciting mechanism, H_2 and O_2 can stay at room temperatures indefinitely without forming H_2O . As the temperature increases more and more energy is available to lift these molecules to their activated state. Activation obviously results from the collisions of molecules whose velocities are in the high-energy tail of the Maxwellian distribution of molecular velocities. Hence, the reaction rate increases rapidly with increasing temperature. In the case of dissociation of NO_2 into NO and O_2 , the energy of activation is about 30,000 calories per mole, or 1.3 electron volts per molecule. This high value renders NO_2 stable at temperatures below 370°K ; but it starts to dissociate at an appreciable rate at 450°K . In the case of dissociation of NO into N_2 and O_2 , the energy of activation for the dissociation process is even higher, although the precise value has not been determined. Consequently it would be expected that NO would start to dissociate at an even higher temperature than the dissociation temperature of NO_2 . Indeed, the reaction given by Equation 2 starts at temperatures around 1000°K . Therefore, it can be concluded that NO_2 is stable at temperatures below 370°K . This covers the range of temperatures prevailing in the atmospheres of Mars and Jupiter, but it may not account for all temperatures in the lower atmosphere of Venus (Reference 2). However, because of the barrier provided by NO^* , nitric oxide will not decompose into N_2 and O_2 even in the latter atmosphere.

DECOMPOSITION OF NO_2

The stability of NO_2 , just discussed, is only for time scales encountered in the chemical laboratory. Further examination must be made to determine whether it is valid for astronomical time scales. For, although the rate of reaction decreases rapidly

with the lowering of temperature, in reality it never vanishes. Thus, a reaction proceeds even at low temperatures, though very slowly. This situation can be compared with the evaporation of stars from a cluster. Over a short period of time the cluster appears to be in a state of equilibrium, but for a time scale of a few billion years the cluster is losing stars continually. The two problems become physically identical if we examine their underlying reason. Stars which escape from a cluster have velocities which are in the high-energy tail of the Maxwellian distribution of stellar velocities, whereas a chemical reaction proceeds at low temperatures because of the molecules have velocities in the high-energy tail of the Maxwellian distribution of molecular velocities.

The rate of a chemical reaction is determined, aside from consideration of the concentrations of reactants, by the velocity constant

$$k = Z \exp \left(\frac{-E}{RT} \right) , \quad (3)$$

where E is the energy of activation, R is the gas constant, T is the temperature in $^{\circ}\text{K}$, and Z is a factor resulting from the consideration of molecular collisions. Although Z depends also upon T , its dependence is rather weak compared with that of the exponential factor in Equation 3. Therefore in a first approximation Z may be considered a constant. Since the time, τ for a reaction to take place is inversely proportional to k , i.e.,

$$\tau \propto \frac{1}{k} , \quad (4)$$

the time scales τ_1 and τ_2 of the same reaction, under the same conditions except a temperature difference, should have a ratio given by

$$\frac{\tau_1}{\tau_2} = \exp \left[\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right] . \quad (5)$$

Unfortunately the value of E is unknown especially for the reaction given by Equation 2. Since this reaction occurs only at temperatures of about 1000°K , it may be reasonably estimated that E in this case is of the order of 60,000 calories per mole, or 2.6 electron volts per molecule. Then if $T_1 = 293^{\circ}\text{K}$ and $T_2 = 1000^{\circ}\text{K}$,

$$\frac{\tau_1}{\tau_2} = 5 \times 10^{31} . \quad (6)$$

Even if τ_2 is a fraction of a second, τ_1 would still be much longer than the age of our galaxy. Therefore we may conclude that if nitrogen peroxide is formed in the atmosphere of a planet, it will stay there indefinitely if no activation mechanism other than thermal collision is available.

HOW NITROGEN PEROXIDE IS FORMED IN ATMOSPHERES

There would seem to be two possible explanations for the formation of the nitrogen peroxide: (1) by thermal process in the early days of a planet's history, when the temperature is high; or (2) by a special activation mechanism which operates under the present conditions.

Figure 1 shows that the first possibility is impracticable. When the temperature is high enough that nitrogen and oxygen combine to form oxides of nitrogen, other reactions will also take place. Then formation of thermodynamically stable molecules, i.e., those having negative free energies of formation, will be favored. Thus, a nitrogen-oxygen-hydrogen mixture with some carbon will produce, dominantly, H_2O , NH_3 , CO_2 , CH_4 , etc. The only alternative to this conclusion would seem to be that the atmosphere contained no hydrogen — an unlikely explanation since hydrogen is the dominant element in the universe. However, for the atmospheres of Mars and Venus, a lack of hydrogen could still be explained by its easy escape from the atmospheres. But according to Kiess and his collaborators, the spectral bands of Mars and Venus which were identified by them as due to nitrogen peroxide are also present in the spectra of Jupiter. It would scarcely be denied that hydrogen has always been present in Jupiter's atmosphere; therefore, it would be difficult to suggest that NO_2 is formed in this way in the atmosphere of Jupiter.

Now consider the second possibility. In order to form nitrogen peroxide under conditions now prevailing in the atmospheres of the planets, there must be some activation mechanisms present in the form of ultraviolet light or high-energy particles from the sun. A mixture of nitrogen and oxygen under ultraviolet or corpuscular radiation can produce some nitrogen peroxide. Indeed, photoionization of molecules of nitric oxide has been proposed to explain the D region in the earth's atmosphere, although no direct observational evidence concerning the molecules in these high layers has been obtained to date (Reference 3). On the other hand, the mechanism which can activate N_2 and O_2 to form NO , and consequently NO_2 and N_2O_4 , can also activate the products and make them dissociate into N_2 and O_2 . In such a case it would be expected that the relative abundances of NO , NO_2 , N_2O_4 , N_2 , and O_2 would follow, roughly, the equilibrium distribution, which could be easily calculated from the dissociation constants of three chemical

reactions involving these molecules. The following dissociation constants have been given by Kelley (Reference 4) for different temperatures:

$$K_1 = \frac{p_{\text{NO}}^2 p_{\text{O}_2}}{p_{\text{NO}_2}^2} ; \quad (7)$$

$$K_2 = \frac{p_{\text{N}_2} p_{\text{O}_2}^2}{p_{\text{NO}_2}^2} ; \quad (8)$$

$$K_3 = \frac{p_{\text{N}_2\text{O}_4}}{p_{\text{NO}_2}^2} , \quad (9)$$

where p_X denotes the partial pressure of the particular molecular species X in equilibrium. From the values of these constants it is possible to compute the partial pressures of different molecular species in a mixture of nitrogen, oxygen, and their compounds. Table 1, which is plotted in Figure 2, gives the results of calculations for the case when the total pressure is one atmosphere and the nitrogen to oxygen abundance ratio is the same as that of the earth's atmosphere. It is clear from this example what a small amount of the nitrogen oxides exists in the mixture. The earth's atmosphere is

Table 1
Equilibrium Partial Pressures of NO, NO₂ and N₂O₄ at Different Temperatures

Temperature (°K)	Pressure (atmospheres)		
	NO	NO ₂	N ₂ O ₄
298.2	2.99×10^{-16}	1.89×10^{-10}	2.42×10^{-18}
400	3.11×10^{-12}	5.65×10^{-9}	5.73×10^{-17}
500	7.02×10^{-10}	4.06×10^{-8}	1.04×10^{-16}
600	2.61×10^{-8}	1.49×10^{-7}	1.53×10^{-16}
700	3.46×10^{-7}	3.77×10^{-7}	2.12×10^{-16}
800	2.40×10^{-6}	7.52×10^{-7}	2.67×10^{-16}
900	1.08×10^{-5}	1.30×10^{-6}	3.35×10^{-16}
1000	3.62×10^{-5}	2.00×10^{-6}	4.00×10^{-16}

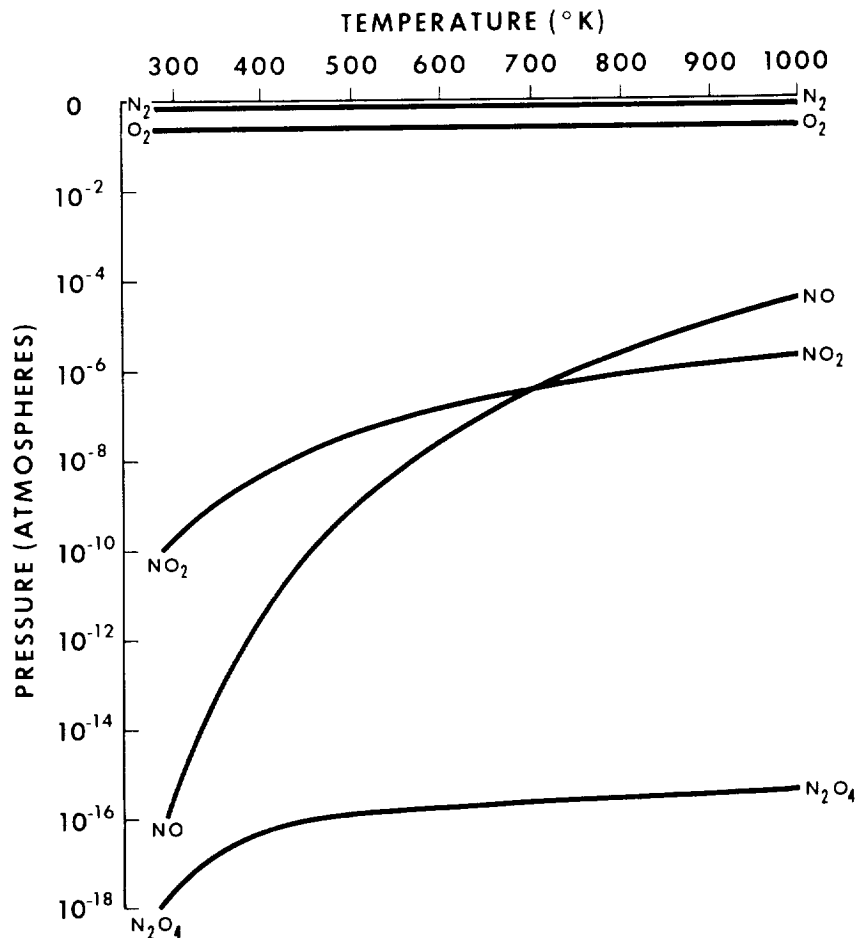


Figure 2 — The equilibrium pressures of N_2 , O_2 , NO , NO_2 and N_2O_4 at different temperatures. The total pressure is one atmosphere and the nitrogen to oxygen abundance ratio is assumed to be the same as is found in the earth's atmosphere.

still dominantly oxygen and nitrogen; but oxygen has never been observed in the atmospheres of Mars, Venus, or Jupiter. This makes the hypothesis of activation by radiation impracticable.

CONCLUSION

When everything is considered, it appears that the formation of nitrogen peroxide in the atmospheres of planets encounters serious difficulties, as does any theory which has been put forth to answer these difficulties. Indeed, recent papers by Sinton and others (References 5 and 6) raise the question of the validity of the interpretation made by Kiess and his collaborators.

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